

Chapter 13 - Polymers Introduction

I. Nomenclature

A. Polymer/Macromolecule

polymer - nonmetallic material consisting of large molecules composed of many repeating units

- from Greek: poly (many) and meros (parts); built from one (mons) part (meros)
- also referred to as macromolecules
- can exist both in natural and synthetic form

B. Examples of Polymers

Natural Polymers

wood
cotton
silk
wool
leather
starch
rubber
proteins
DNA (deoxyribonucleic acid)
RNA (ribonucleic acid)

Synthetic Polymers

"plastics"
adhesives
epoxies
"rubber"

C. Classification of Synthetic Polymers

Types:

Thermoplastics
Thermosets
Elastomers

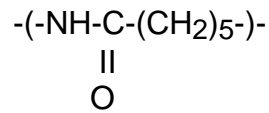
Thermoplastics:

- usually linear or branched structures which soften and may flow at elevated temperatures. At these temperatures, with "melting":
 - * no chemical change occurs (no degradation etc)
 - * no bonds are actually broken
 - * changes in bonding between chains (intermolecular or secondary bonds); contributing to a reduction in viscosity
 - * broken secondary bonds allow for chains to more easily past one another.

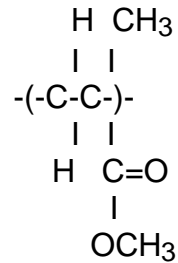
Examples of thermoplastics:

PE	nylon
PS	PMMA
PP	Teflon (PTFE)
PVC	PET (a polyester)
PC	POM (polyacetal)

nylon - polycaprolactam; nylon 6 ("Nylon" is a generic name.
Nylons are of the group of polymers called **polyamides**.)



polymethylmethacrylate
(PMMA); Plexiglas, Lucite



Thermosets:

- crosslinkable systems which are formed initially in a flowable stage and then "set" into crosslinked, intractable non-melting systems by the application of heat and pressure.
- can't be softened again without chemical decomposition (irreversible hardening)
- usually very brittle and hard.

Examples of thermosets:

phenolic - phenol-formaldehyde (Bakelite)
epoxy - EPON
unsaturated polyesters
melamine-formaldehyde
polyurethane

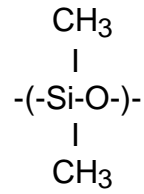
Rubbers/Elastomers:

Rubber: natural polymer; a linear polymer which can be stretched to at least two times its original length when force is applied and will return rapidly and forcibly to its original dimensions when the force is removed.

Elastomer: "rubbery-like" material, from the standpoint of modulus. That is, it has a similarly low modulus (under 100 kpsi). But, one that has **limited extensibility** and **does not** exhibit complete retraction.

Examples:

natural rubber-cis 1,4 - polyisoprene
styrene butadiene styrene (SBS)
polybutadiene
polychlororene - neoprene
silicone rubber - poly(dimethyl siloxane)



II. Molecular Structure

A. Linear

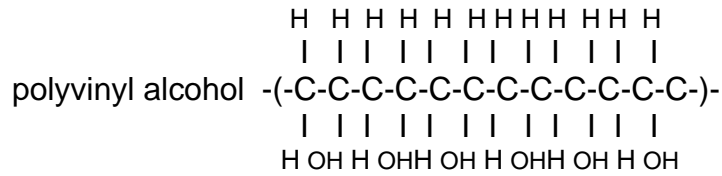
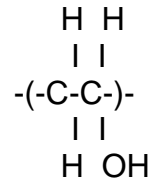
linear - large one dimensional molecules (chains)
 - thermoplastics, elastomers are of this kind

Homopolymer - one type of repeat unit on the chain

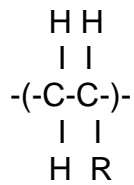
- polymer built from a single monomeric species

AAAAAAAAAAAAA


where A represents
 a repeat unit such as:



Other types of vinyl molecules:



where R represents a substituent group of atoms, thus:

<u>R</u>	<u>polymer</u>
H	polyethylene (PE)
OH	polyvinyl alcohol (PVA)
Cl	polyvinyl chloride (PVC)
CH ₃	polypropylene (PP)
	polystyrene (PS)
O-C=O-CH ₃	polyvinyl acetate
C≡N	polyacrylonitrile (PAN)

Copolymers - more than one type of repeat unit on the chain.
Made by chemical combination of two or more different monomeric species.

Example: ABS acrylonitrile - butadiene - styrene; HIPS; SBS

Not the same as a blend (not one chain mixed with another)

Random Copolymer - a copolymer with no systematic repetition different monomeric species.

If A and B represent different repeat units, then a random copolymer has this chain structure:

AABABBBAAABBABA

Block Copolymer: a copolymer where monomeric species are arranged in groups along the chain.

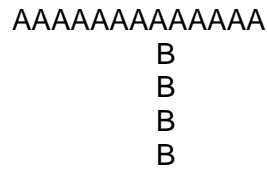
Example: AAABBBBBBCCCCCAABB

B. Branched Polymers

Homopolymer - all one type of monomer. For example, polyethylene branches substantially if allowed to. This tends to reduce the crystallinity (increase the free volume)

AAAAAAAAAAAAAAAAA
A
A
A
A

Branched/Graft Copolymer:



C. Crosslinked or Network Polymers

Crosslinking - primary (normally covalent) bonding between polymer chains. These bonds are very strong covalent bonds (not weak Van der Waals secondary bonds). An example of crosslinking is the vulcanization of rubber, where sulfur forms the crosslinks.

Thermosetting polymers might be classified as having chains which are infinitely crosslinked.

Network Polymer - covalent bonds throughout (3-D), in all directions (not crystalline in any sense) - infinitely crosslinked (Thermosets - in the end we end up with really one molecule.)

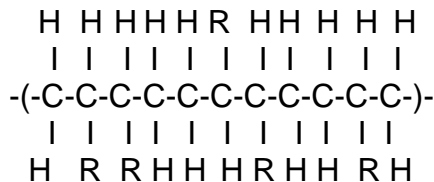
III. Stereoregularity

stereoregularity
 stereospecific
 stereoisomers

} → terms concerned with spatial regularity in polymer chain

A. Atactic

- "without any repetitive nature"
- e.g. polypropylene can be atactic.

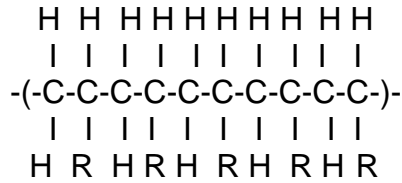


no regular placement of pendant group, R.
 For polypropylene, the R group is CH₃.

However, Ziegler-Natta catalysis is used to produce PP which is not atactic, but displays stereoisomerism.

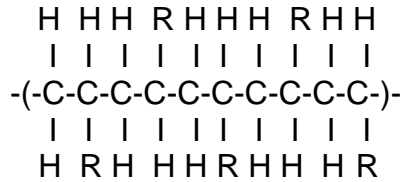
B. Isotactic

- R group is always in the same position



C. Syndiotactic

- alternating arrangement of the substituent group



IV. Chain Morphology

A. Amorphous

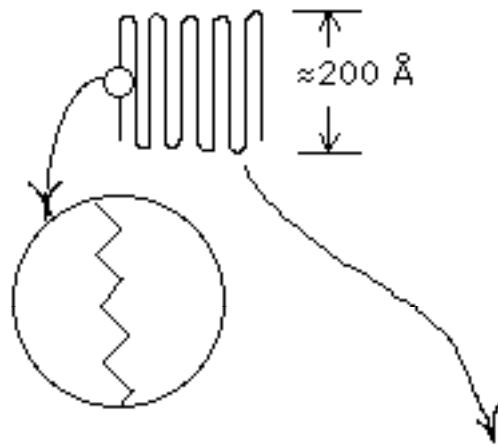
- polymers which have no structural order between chains
- usually composed of units which have large side groups, or they are non-uniform and the molecules can not realign themselves in an ordered arrangement.

Example: PS, PMMA, PC, PVC

- "can of worms" model

B. Crystalline

- polymers that are characterized by the capability of their molecules to form 3-D ordered arrays.
- chain folding

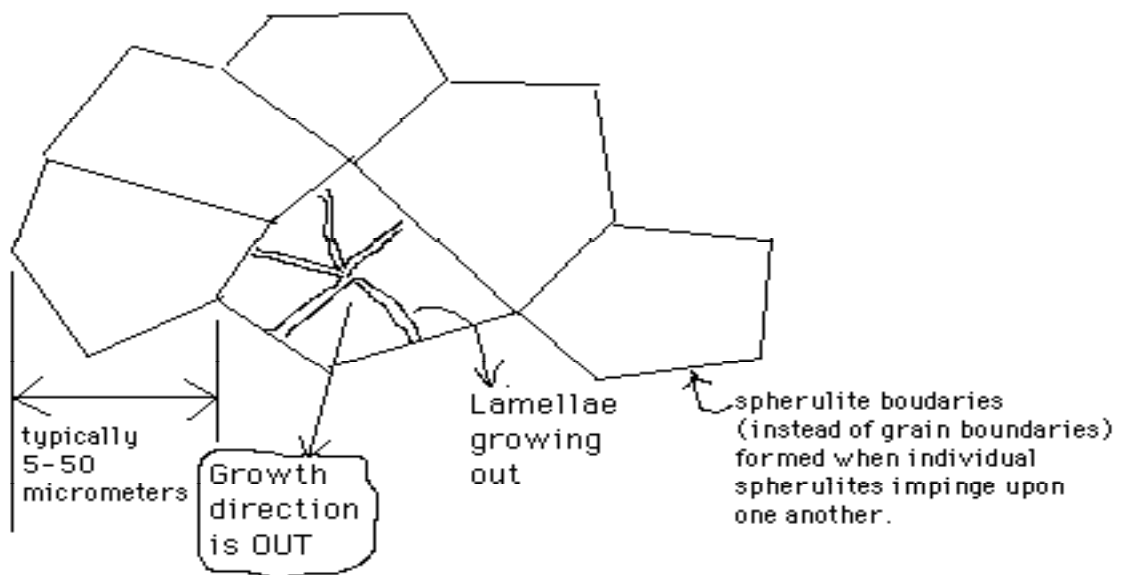


form thin lamella which acts as a single crystal - called a crystallite. Interaction occurs between lamellae.

- crystalline polymers are denser, stronger, and tougher than amorphous polymers.

Examples: PE, PP, PET, nylons, PTFE, POM

* Actually, these polymers aren't completely crystalline. Therefore, semicrystalline polymers are composed of crystalline portions and amorphous portions.



Amorphous material occupies regions between crystallites